

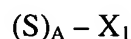
CLAIMS:

The claimed inventions are:

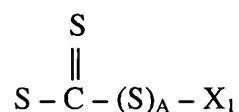
1. A process for preparing roughened copper surfaces suitable for
5 subsequent multilayer lamination, said process comprising the steps of:

contacting with a clean copper surface an adhesion promoting composition under
conditions effective to provide a roughened copper surface, said adhesion
promoting composition comprising an oxidizer, a pH adjuster, and a topography
10 modifier; and

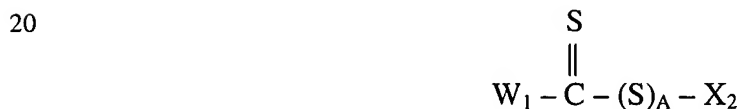
contacting said roughened copper surface with an acid resistance promoting
composition having a formula selected from the group consisting of:



- 15 wherein **A** is 1-20 and wherein **X₁** is Mg, Ca, Li₂, Na₂, K₂, or (NH₄)₂;



wherein **A** is 1-20 and wherein **X₁** is Mg, Ca, Li₂, Na₂, K₂, or (NH₄)₂; and



- 25 wherein **W₁** is $\begin{array}{c} R_1 \\ / \\ N \\ \backslash \\ R_2 \end{array}$, O-R₃, or S-R₃, wherein **A** is 1-20, wherein **X₂** is Li,

Na, K, NH₄, Mg – (S)_B – $\overset{\text{S}}{\parallel}\text{C}$ – W₂, or Ca – (S)_B – $\overset{\text{S}}{\parallel}\text{C}$ – W₂, wherein W₂ is

5 $\begin{array}{c} \text{R}_4 \\ / \\ \text{N} \\ \backslash \\ \text{R}_5 \end{array}$, O–R₆, or S–R₆, wherein B is 1-20, and wherein R₁₋₆ are

10 independently selected from H and halogen, or wherein R₁₋₆ are independently selected from, or any two adjacent R₁₋₆ can be a linkage comprising S, epoxide, glycol, hydroxy, aryloxy, benzyloxy, alkoxy, haloalkoxy, amino, monoalkylamino, dialkylamino, heteroalkylamino, acyloxy, acyl, ketone, 15 quinone, aldehyde, carbohydrate, organometallic, a C₁ up to C₁₈ alkyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a cycloalkyl which may be singly or multiply substituted in singular or multiply bonded fashion, a heterocyclic which may be singly or multiply substituted in singular or multiply bonded fashion, a C₁ up to C₁₈ alkenyl 20 which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a C₁ up to C₁₈ alkadienyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a C₁ up to C₁₈ alkynyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, an aryl which may be singly or 25 multiply substituted in singular or multiply bonded fashion, a heteroaryl which may be singly or multiply substituted in singular or multiply bonded fashion, an alkylaryl which may be singly or multiply substituted in singular or multiply bonded fashion, an arylalkyl which may be singly or multiply substituted in

singular or multiply bonded fashion, and combinations thereof, wherein the substituents are selected from the group consisting of halogen, epoxide, glycol, N, O, S, haloalkyl, hydroxy, aryloxy, benzyloxy, alkoxy, haloalkoxy, amino, monoalkylamino, dialkylamino, heteroalkylamino, acyloxy, acyl, ketone, quinone, aldehyde, carbohydrate, organometallic, alkyl, aryl, and combinations thereof.

2. The process according to claim 1, wherein said acid resistance promoting composition is selected from the group consisting of sodium dioctyldithiocarbamate, disodium trithiocarbonate, sodium sulfide, sodium N,N-dibutyldithiocarbamate and sodium hydroquinone monomethyl ether xanthate.

3. The process according to claim 2, wherein said acid resistance promoting composition is sodium sulfide.

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4. The process according to claim 1, wherein A is 1-5.

5. The process according to claim 1, wherein the step of contacting said roughened copper surface with said acid resistance promoting composition is carried out in an aqueous solution.

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6. The process according to claim 5, wherein said acid resistance promoting composition is present in said aqueous solution in the range between about 0.1 g/l and about 5 g/l.

5 7. The process according to claim 6, wherein said acid resistance promoting composition is present in said aqueous solution in the range between about 1 g/l and about 3 g/l.

8. The process according to claim 7, wherein said acid resistance
10 promoting composition is present in said aqueous solution at about 1 g/l.

9. The process according to claim 1, wherein said acid resistance promoting composition is contacted with said roughened copper surface for between about 1 second to about 5 minutes.

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10. The process according to claim 9, wherein said acid resistance promoting composition is contacted with said roughened copper surface for between about 5 seconds to about 2 minutes.

20 11. The process according to claim 1, wherein said acid resistance promoting composition is contacted with said roughened copper surface for at least about 1 second.

12. The process according to claim 1, wherein said clean copper surface is pretreated with a pretreatment composition comprising an oxidizer, a pH adjuster and a topography modifier.

5 13. The process of claim 12, wherein said oxidizer in said pretreatment composition is hydrogen peroxide.

14. The process of claim 13, wherein said pretreatment composition further comprises a hydrogen peroxide stabilizer.

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15. The process according to claim 1, wherein said process is preceded with the optional steps of:

providing a substantially clean copper surface;

providing a pretreatment composition comprising an oxidizer, a pH
15 adjuster and a topography modifier; and

contacting said substantially clean copper surface with said pretreatment composition under conditions effective to provide a clean copper surface.

16. A process according to claim 1, further comprising the step of
20 rinsing said roughened copper surface with water prior to contacting the surface with said acid resistance promoting composition.

17. The process according to claim 1, wherein said adhesion promoting composition further comprises at least one of a uniformity enhancer and a coating promoter.

5 18. The process according to claim 1, wherein said oxidizer in said adhesion promoting composition is hydrogen peroxide.

19. The process according to claim 18, wherein said adhesion promoting composition further comprises a hydrogen peroxide stabilizer.

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20. The process according to claim 19, wherein said hydrogen peroxide stabilizer is sodium phenolsulfonate.

21. The process according to claim 1, wherein said pH adjuster in said
15 adhesion promoting composition is selected from the group consisting of sulfuric acid, phosphoric acid, acetic acid, formic acid, sulfamic acid, and hydroxy-acetic acid.

22. The process according to claim 21, wherein said pH adjuster in
20 said adhesion promoting composition is sulfuric acid.

23. The process according to claim 1, wherein said pH adjuster is present in said adhesion promoting composition in the range between about 0.01% and about 20% by weight.

5 24. The process according to claim 23, wherein said pH adjuster is present in said adhesion promoting composition in the range between about 0.5% and about 10% by weight.

25. The process according to claim 1, wherein said topography
10 modifier in said adhesion promoting composition is a 5-membered aromatic fused N heterocyclic compound, wherein said N heterocyclic ring has a nitrogen atom at position 1 bonded to a hydrogen atom.

26. The process according to claim 25, wherein said 5-membered
15 aromatic fused N heterocyclic compound is selected from the group consisting of 1H-benzotriazole; 1H-indole; 1H-indazole; 1H-benzimidazole; 5-Methyl-1H-benzotriazole; 6-Nitro-1H-benzotriazole; 1H-naphtho(1,2-d)triazole; 1H-Naphtho[2,3-d]triazole; 5-Aminoindole; 6-methylindole; 1H-indole-5-methyl; 7-methylindol; 3-methylindole; 2-Methylindole; 1H-Indole, 3,5-dimethyl-; 2,3-Dimethylindole; 2,6-dimethylindole; 1H-Indazol-5-amine; 3-Chloro-1H-indazole; 2-Hydroxy-1H-benzimidazole; 2-Methyl-1H-benzimidazole; and 2-(methylthio)-
20 1H-benzimidazole.

27. The process according to claim 1, wherein said topography modifier is present in said adhesion promoting composition in the range between about 0.1 g/l and about 20 g/l.

5 28. The process according to claim 27, wherein said topography modifier is present in said adhesion promoting composition in the range between about 0.5 g/l and about 7 g/l.

29. The process according to claim 1, wherein said adhesion
10 promoting composition further comprises a halogen ion.

30. The process according to claim 29, wherein said halogen ion is chloride ion.

15 31. The process according to claim 29, wherein said halogen ion is present in said adhesion promoting composition in the range between about 1 ppm to about 100 ppm.

32. The process according to claim 1, wherein said adhesion
20 promoting composition further comprises a water soluble polymer.

33. The process according to claim 32, wherein said water soluble polymer is present in said adhesion promoting composition in the range between about 0.5 wt% and about 3 wt%.

5 34. The composition according to claim 32, wherein said water soluble polymer is a polyethylene glycol.

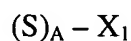
35. A process for preparing roughened copper surfaces suitable for subsequent multilayer lamination, said process comprising the steps of:

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providing an adhesion promoting composition comprising an oxidizer, a pH adjuster, and a topography modifier;

providing an acid resistance promoting composition comprising a formula

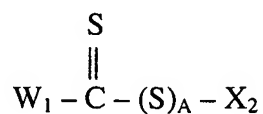
15 selected from the group consisting of:



wherein A is 1-20 and wherein X₁ is Mg, Ca, Li₂, Na₂, K₂, or (NH₄)₂;



wherein A is 1-20 and wherein X₁ is Mg, Ca, Li₂, Na₂, K₂, or (NH₄)₂; and



wherein W_1 is $N \begin{matrix} / & R_1 \\ & \\ \backslash & R_2 \end{matrix}$, $O-R_3$, or $S-R_3$, wherein A is 1-20, wherein X_2 is Li,

Na, K, NH_4 , $Mg - (S)_B - \overset{\overset{S}{\parallel}}{C} - W_2$, or $Ca - (S)_B - \overset{\overset{S}{\parallel}}{C} - W_2$, wherein W_2 is

$N \begin{matrix} / & R_4 \\ & \\ \backslash & R_5 \end{matrix}$, $O-R_6$, or $S-R_6$, wherein B is 1-20, and wherein R_{1-6} are

independently selected from H and halogen, or wherein R_{1-6} are independently selected from, or any two adjacent R_{1-6} can be a linkage comprising S, epoxide, glycol, hydroxy, aryloxy, benzyloxy, alkoxy, haloalkoxy, amino, monoalkylamino, dialkylamino, heteroalkylamino, acyloxy, acyl, ketone, quinone, aldehyde, carbohydrate, organometallic, a C_1 up to C_{18} alkyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a cycloalkyl which may be singly or multiply substituted in singular or multiply bonded fashion, a heterocyclic which may be singly or multiply substituted in singular or multiply bonded fashion, a C_1 up to C_{18} alkenyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a C_1 up to C_{18} alkadienyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a C_1 up to C_{18} alkynyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, an aryl which may be singly or multiply substituted in singular or multiply bonded fashion, a heteroaryl which

may be singly or multiply substituted in singular or multiply bonded fashion, an alkylaryl which may be singly or multiply substituted in singular or multiply bonded fashion, an arylalkyl which may be singly or multiply substituted in singular or multiply bonded fashion, and combinations thereof, wherein the
5 substituents are selected from the group consisting of halogen, epoxide, glycol, N, O, S, haloalkyl, hydroxy, aryloxy, benzyloxy, alkoxy, haloalkoxy, amino, monoalkylamino, dialkylamino, heteroalkylamino, acyloxy, acyl, ketone, quinone, aldehyde, carbohydrate, organometallic, alkyl, aryl, and combinations thereof;

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providing a clean copper surface;

contacting said clean copper surface with said adhesion promoting composition under conditions effective to form a roughened copper surface; and

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contacting said roughened copper surface with said acid resistance promoting composition.

36. The process according to claim 35, wherein said acid resistance
20 promoting composition is selected from the group consisting of sodium dioctyldithiocarbamate, disodium trithiocarbonate, sodium sulfide, sodium N,N-dibutyldithiocarbamate and sodium hydroquinone monomethyl ether xanthate.

37. The process according to claim 35, wherein A is 1-5.

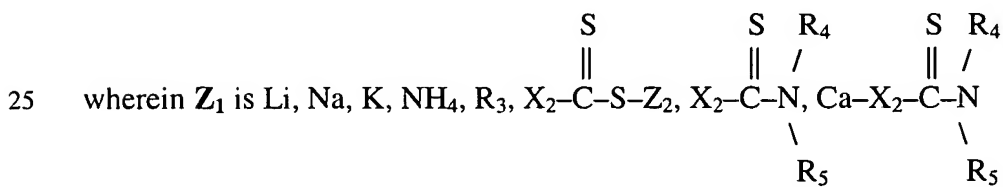
38. The process according to claim 35, wherein the step of contacting
said roughened copper surface with said acid resistance promoting composition is
5 carried out in an aqueous solution.

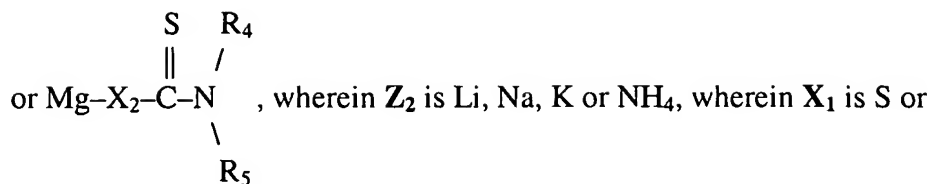
39. The process according to claim 38, wherein said acid resistance
promoting composition is present in said aqueous solution in the range between
about 0.1 g/l and 5 g/l.

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40. The process according to claim 35, wherein said acid resistance
promoting composition is contacted with said roughened copper surface for
between about 1 second to about 5 minutes.

15 41. A copper surface adhesion promoting composition comprising an
oxidizer, a pH adjuster, a topography modifier, and a coating stabilizer having the
formula:





5 N-R₆, wherein X₂ is S or N-R₇, and wherein R₁₋₇ are independently selected from H and halogen, or wherein R₁₋₇ are independently selected from, or any two or more of R₁₋₇ can be a linkage comprising S, epoxide, glycol, hydroxy, aryloxy,

10 benzyloxy, alkoxy, haloalkoxy, amino, monoalkylamino, dialkylamino, heteroalkylamino, acyloxy, acyl, ketone, quinone, aldehyde, carbohydrate, organometallic, a C₁ up to C₁₈ alkyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a cycloalkyl which may be singly or multiply substituted in singular or multiply bonded fashion, a

15 heterocyclic which may be singly or multiply substituted in singular or multiply bonded fashion, a C₁ up to C₁₈ alkenyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a C₁ up to C₁₈ alkadienyl which is linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, a C₁ up to C₁₈ alkynyl which is

20 linear or branched and may be singly or multiply substituted in singular or multiply bonded fashion, an aryl which may be singly or multiply substituted in singular or multiply bonded fashion, a heteroaryl which may be singly or multiply substituted in singular or multiply bonded fashion, an alkylaryl which may be singly or multiply substituted in singular or multiply bonded fashion, an arylalkyl

25 which may be singly or multiply substituted in singular or multiply bonded fashion, and combinations thereof, wherein the substituents are selected from the

group consisting of halogen, epoxide, glycol, N, O, S, haloalkyl, hydroxy, aryloxy, benzyloxy, alkoxy, haloalkoxy, amino, monoalkylamino, dialkylamino, heteroalkylamino, acyloxy, acyl, ketone, quinone, aldehyde, carbohydrate, organometallic, alkyl, aryl, and combinations thereof.

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42. A copper surface adhesion promoting composition according to claim 41, wherein said coating stabilizer is selected from the group consisting of 2-imidazolidinethione; potassium 3-(thiocarbamoyl)-dithiocarbazate; sodium diethyldithiocarbamate; sodium dimethyldithiocarbamate; tetraethylthiuram
10 disulfide; tetramethylthiuram disulfide; and 2,5-dithiobiurea.

43. A copper surface adhesion promoting composition according to claim 42, wherein said coating stabilizer is sodium diethyldithiocarbamate.

15 44. A copper surface adhesion promoting composition according to claim 41, wherein said coating stabilizer is present in the composition in the range between about 1 to about 1000 ppm.

45. A copper surface adhesion promoting composition according to
20 claim 44, wherein said coating stabilizer is present in the composition in the range between about 2 to about 200 ppm.

46. A copper surface adhesion promoting composition according to claim 45, wherein said coating stabilizer is present in the composition in the range between about 50 to about 150 ppm.